OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/
HONORS/STUDENT REPORT

for

CONTRACT N00014-90-J-1156

R&T Code 4133042

# Novel Electrochemical Materials Prepared by Sol-Gel Chemistry

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# OFFICE OF NAVAL RESEARCH
# PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 4133042
Contract/Grant Number: N00014-90-J-1156
Contract /Grant Title: Novel Electrochemical Materials Prepared by Sol-Gel Chemistry
Principal Investigator Gregory C. Farrington

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a. Number of papers submitted to refereed journals, but not published:__9__
b. * Number of papers published in refereed journals **(for each, provide a complete citation)**:__3_
c. Number of books or chapters submitted, but not yet published:__2__
d. * Number of books or chapters published **(for each, provide a complete citation)**:__0__
e. * Number of printed technical reports/non-refereed papers **(for each, provide a complete citation)**:__0__
f. Number of patents filed:__0__
g. * Number of patents granted **(for each, provide a complete citation)**:__0__
h. * Number of invited presentations **(for each, provide a complete citation)**:__7__
i. * Number of submitted presentations **(for each, provide a complete citation)**:__7__
j. * Honors/Awards/Prizes for contract/grant employees *(list attached)*:__9___
k. Total number of **Full-time equivalent** Graduate Students and Post Doctoral associates supported during this period, under this R&T project number:
   Graduate Students: 6
   Post-Doctoral Associates: 1
  including the number of,
   Female Graduate Students: 2
   Female Post Doctoral Associates: 0
  the number of
   Minority* Graduate Students: 0
   Minority* Post Doctoral Associates: 0
  and, the number of
   Asian Graduate Students: 2
   Asian Post Doctoral Associates: 0

l. * Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

* Use the letter and an appropriate title as a heading for your list, e.g.:
  b. Published Papers in Refereed Journals, or, d. Books and Chapeters published
  Also submit the citation lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disk

*Minorities include Blacks, Aleuts, Amindians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

## PART I

a. Number of papers submitted, but not published: 9

1. J. Sjöblom, M. Selle, S. E. Friberg, T. Moaddel, C. Brancewicz, "Hydrolysis and Condensation of Octyltrimethoxy Silane in Nonionic Liquid Crystal," *Colloids and Surfaces*, (submitted)

2. B. Ammundsen, G. R. Burns, A. Amran, S. E. Friberg, "Silica and Supported Spinel $LiMn_2O_4$ from Microemulsion-Derived Multicomponent Gels," *J. Sol/Gel Synth. Proc.* (in press)

3. B. Ammundsen, G. R. Burns, A. Amran, S. E. Friberg, "A Study of the Formation of Silica-Supported Mixed Magnesium-Manganese Spinel Oxides from Multicomponent Gels," *J. Sol/Gel Synth. Proc.* (in press)

4. S. E. Friberg, A. Amran, J. Sjöblom, "Reaction Between Aluminum Nitrate Nanohydrate and Tetraethoxysilane in Ethanol," *J. Non-Cryst. Solids*, (submitted)

5. S. E. Friberg, J. Yang, J. Sjöblom, G. Farrington, "Reaction Between Copper Nitrate Hydrate and Tetraecthoxysilane in Methanol, a $^{29}Si$ NMR Investigation," *J. Phys. Chem.* (submitted)

6. S. E. Friberg, S. Jones, G. Broze, A. Motyka, "Viscoelastic Microemulsion - Gels," *J. Material Sci.* (in press)

7. B. Amumundsen, G. R. Burns, A. Amran, S. E. Friberg, "Silica and Supported Spinel $LiMn_2O$- from Microemulsion-Derived Multicomponent Gels," *J. Sol/Gel Synth. Proc.* (in press)

8. S. M. Jones, S. E. Friberg, J. Sjöblom, "A Bioactive Composite Material produced by the Sol/Gel Method," *J. Material Sci.* (in press)

9. "Sol-Gel Approaches for Solid Electrolytes and Electrode Materials," B. Dunn, G. C. Farrington and B. Katz, *Solid State Ionics*, to appear

b. Number of papers published: 3

1. S. E. Friberg, C.C. Yang, "Limitations of the So/Gel Process with Aluminum Nitrate," *Particulate Sci. and Techn.* 11, 1 (1993)

2. J. Sjoblom, H. Ebeltoft, A. Bjorseth, S. F. Friberg, C. Brancewicz, "Hydrolysis and Condensation of Alkyltrimethoxysilancs in Monomolecular Fiims," *J. Disp. Sci Tech.* 15, 21 (1994)

3. S. M. Jones, A. Amran, S. E. Friberg, J. Sjoblom, "Microemulsion Gel Glass Containing Copper Nitrate," *J. Disp. Sci. Techn.* 15, 513 (1994)

c. Number of books or chapters submitted: 2

1. S. E. Friberg, J. Sjöblom, "The Microemulsion/Gel Process" in *Applications of Microemulsions*, (C. Solans, ed.), Marcel Dekker

2. S. E. Friberg, "Microemulsion/Gel Method" in *Sol-Gel Processing and Application*, (Y. A. Attia, ed.), Plenum Press (in press

d. Number of books or chapters published: 0

e. Number of printed technical reports/non-refereed papers: 0

f. Number of patents filed: 0

g. Number of patents granted: 0

h. Number of invited presentations: 7

1. S. Friberg, University of Bergen, Bergen Norway, "Colloidal Chemistry in Materials Science," July, 1993

2. S. Friberg, Fine Particles Symposium, Society of Cosmetics Chemists, Chicago, IL., "Gelation of Water-in-Oil Microemulsions," August, 1993

3. S. Friberg, Montefluos, Bollate, Milano, Italy, "Extension of the Sol/Gel Process into Colloid Chemistry: Some New Reactions,: October, 1993

4. S. Friberg, University of Bergen, Bergen, Norway, "Sol/Gel Process with Hydrated Metal Salts, " November, 1993

5. S. Friberg, Glaxo, Research Triangle Park, NC, "Nano-sized Particles from Microemulsions and Liquid Crystals," March, 1994

6. J. Linde, D. Brown and J. O. Thomas, "Molecular Dynamics Simulation of Intercalation Effects in Vanadium Pentoxide Gel," The 6th International Conference on the Structure of Non-Crystalline Materials. Prague, August 1994

7. G.C. Farrington, B. Katz, W. Liu, and B. Dunn, "Sol-Gel Preparation of $V_2O_5$-based Electrochemical Materials," International Symposium on Solid State Ionics, Warsaw, Poland, May 1994

i. Number of submitted presentations: 7

1. American Chemical Society National Symposium, Chicago, IL, August 1993, "The Microemulsion/Gel Method," S. Friberg

2. Stanford Symposium, Stanford, CA, June 1994, "Formation of Solid Particles of Copper Salts in a Lyotropic Liquid Crystal," S. Friberg

3. Stanford Symposium, Stanford, CA, June 1994, "Inorganic Polymers Formed in W/O Microemulsions," S. Friberg

4. 10th International Symposium on Surfactants in Solution, Caracus, Venezuala, June 1994, "The Microemulsion/Gel Process," S. Friberg

5. Gordon Conference, New London, NH, July 1994, "SSI Materials By Sol-Gel Methods" B. Dunn, F. Chaput, B. Katz and W. Liu

6. International Conference on Solid State Ionics Conference, The Hague, Netherlands, September 1993, "Sol-Gel Approaches for Solid Electrolytes and Electrode Materials, " B. Dunn, G. C. Farrington and B. Katz,

7. Electrochemical Society, Honolulu, Hawaii, May 1993, "Electrical and Electrochemical Characterization of Vandium Pentoxide Xerogels" by B. Katz, I. Mann, L. Xie and G. C Farrington

j. Honors/Awards/Prizes for contract/grant employees: 9

Stig Friberg: received D. Sci. (Honorary), Åbo Academy University, Finland, 1993

Stig Friberg Member of the International Advisory Board of the Colloid Journal of the Russian Academy of Sciences

Stig Friberg: Member of the Editorial Board of the Advances in Colloid and Interface Science

Stig Friberg: Chairman of the American Chemical Society, 70th Colloid and Surface Science Symposium, 1996

J. O. Thomas: Editorial Boards of Journal of Solid State Ionics and Journal of Materials Chemistry

J.O. Thomas: Chair, Gordon Conference on Solid State Ionics, June 1994

G.C. Farrington: Chair, International Symposium on Polymer Electrolytes, Newport, RI, June 1994

G.C. Farrington, Scientific Committee of Asian Conference on Solid State Ionics, Kuala-Lumpur, August 1994

G. C. Farrington: International Board of Trustees, Moscow State Technological University, Moscow, Russia

k. Total number of full time equivalent graduate students and postdoctoral associates supported during this period, under this R&T project number: 7

graduate students - 6
postdoctoral fellows - 1
female graduate students - 2

l. Other funding:

S. Friberg: Teledyne, 12964 Panama Street, Los Angeles, CA 90066
"Low Temperature Glass Seal Repair" ($35,000)

S. Friberg: Babcock & Wilcox, P. O. Box 11165, Lynchburg, VA 24506-1165
"Continuous Fiber Ceramic Composites" ($20,000)

J. Thomas: Swedish Science Research Council, partial support for one full Ph.D. and two 50% positions.

G. C. Farrington: National Science Foundation, MRL Program ($39,510)

# PART II

a. Principal Investigator: Gregory C. Farrington
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c. Cognizant ONR Program Manager: Dr. Robert J. Nowak, Chemistry and Physics Division, ONR 331, Office of Naval Research, Ballston Commons, Tower One, Room 503, 800 North Quincy Street, Arlington, VA 22217-5660

d. Description of project: This program is directed at preparing and characterizing novel gels, xerogels, and aerogels which, because of their conductivity and/or charge storage capability, have unusual electrochemical characteristics. Typical materials of interest are the transition-metal oxides currently being exploited in their polycrystalline forms in the electrodes of the lithium batteries. Characterization involves structural and electrochemical studies, atomic force microscopy, and novel X-ray diffraction and μ-FTIR techniques. One of several novel contributions of this work is the use of molecular dynamics simulation as a powerful source of insight into surface and bulk mechanisms in sol-gel synthesized materials.

3. Significant results during last year:

(1) The potential and limitations of the microemulsions/gel process have been established, demonstrating its feasibility to prepare highly conductive materials in the form of proton carriers in a continuous oxide matrix. For example, glasses have been prepared with up to 50% content of concentrated sulfuric acid and ionic conductivities at room temperature in the range of $10^{-3}$ S/cm.

(2) In the total absence of an appropriate MD program for gel simulation, such a program has been written specifically for transition-metal oxide layered structures, and successfully tested for crystalline $V_2O_5$. Current efforts focus on converting this to a realistic model of the gel phase, and analyzing its resulting structural and dynamical features This work proceeds in conjunction with experimental studies; a synthetic facility has been created, and appropriate analytical diffraction techniques developed to monitor the structural changes occurring as water, solvent and salt ions enter and leave the gel under controlled temperature and atmospheric conditions. (Uppsala)

(3) Solvent exchange reactions between the organic solvent propylene carbonate and the interlayer water molecules of vanadium pentoxide xerogels have been found to affect both their morphology and electrochemical lithium intercalation behavior. Investigations into the morphology of dip coated vanadium pentoxide xerogel coatings using the scanning electron microscope and atomic force microscope have been carried out. Results indicate gels that resist propylene carbonate exchange have very different electrochemical lithium intercalation behavior in a lithium perchlorate, propylene carbonate electrolyte compared to those that do not. (Penn and Penn/Uppsala)

(4) Aerogels have extremely low densities and very large surface areas. They are formed from ordinary gels by supercritical extraction of the gelling liquid to leave tenuous network of structural units interspersed with air-filled pores of micron size. Recently, vanadate aerogels have been successfully synthesized in the research group of B. Dunn at UCLA. These materials have considerable electronic conductivity and are of considerable interest for their electrochemical charge storage and catalytic properties. This program has worked in collaboration with his research effort to characterize the structures and chemical and electrochemical characteristics of these unusual new materials. SEM, TEM, and electron diffraction studies show that at low temperatures (RT-220°C), the aerogel structure is a polycrystalline and composed of twisted, filmy-like fibers randomly stacked without prefered orientation. As the temperature is increased, the fiber morphology gradually changes and ultimtely crystallizes. (Penn and Penn/UCLA)

f. Summary of plans for next year's work:

(1) The fundamentals of the colloidal problems connected with the microemulsion/gel process have now been clarified and it has been demonstrated that the problems with the retained organic materials from sufactants may be avoided. Hence, with the potential of protonic conductance now established, the next year will be devoted to the preparation of electronically conducting materials. Preliminary experiments have shown the potential of including large amounts of nonelectrolyte into silica glass; at present different combinations are evaluated. (Clarkson and Clarkson/Penn)

(2) Extensive and systematic diffraction studies will provide a clearer picture of the true nature of the gel structures at the atomic level (much of the current wisdom in the field is based on surprisingly flimsy experimental evidence. Gels will be studied at different temperatures, and containing different amounts of water, solvent and salt. A better understanding of practical size, shape and orientation concepts must emerge.

Systematic $\mu$-FTIR techniques will be employed to study vibrational properties within the gel. It is particularly important to be able to distinguish between surface and bulk features and, in this connection, space-resolved techniques can make a valuable contribution, possibly in combination with H/D substitution.

Correspondence must be achieved between experiment and MD simulations. It is anticipated that a structural model will emerge to explain the stepwise intercalation of water into the $V_2O_5$ gel system. Some progress will also be made in understanding the gel-polymer interface through the simulation of appropriate model systems. (Uppsala and Uppsala/Penn)

(3) Some of the most unusual sol-gel derived materials are the aerogels of $V_2O_5$. These materials have extraordinarily low densities and high surface areas. Characterization studies will focus on understanding the structures of $V_2O_5$ aerogels, their hydration reactions and structural transformations, and their electrochemical characteristics. (Penn)

g. Names of grad. students and postdoctoral(s) currently working on the project: 7

Clarkson:
Abeer Al-Bawaab - Graduate Student
Daniel Heenan - Graduate Student
Jun Yang - Post Doc

Penn:
Bruce Katz - Graduate Student
Wen Liu - Graduate Student

Uppsala:
Jonas Linde - Graduate Student (50% support)
Anna Andersson - Graduate Student (50% support)

PART III

# New Electrochemical Materials via the Microemulsion/Gel Process

## Earlier Technology

- Traditional sol-gel process forms glasses by reacting silica-organic compounds with water in ethanol.

- Disadvantage is that inorganic electrolytes cannot be introduced into the glasses because of their low solubility in ethanol.

## New Process

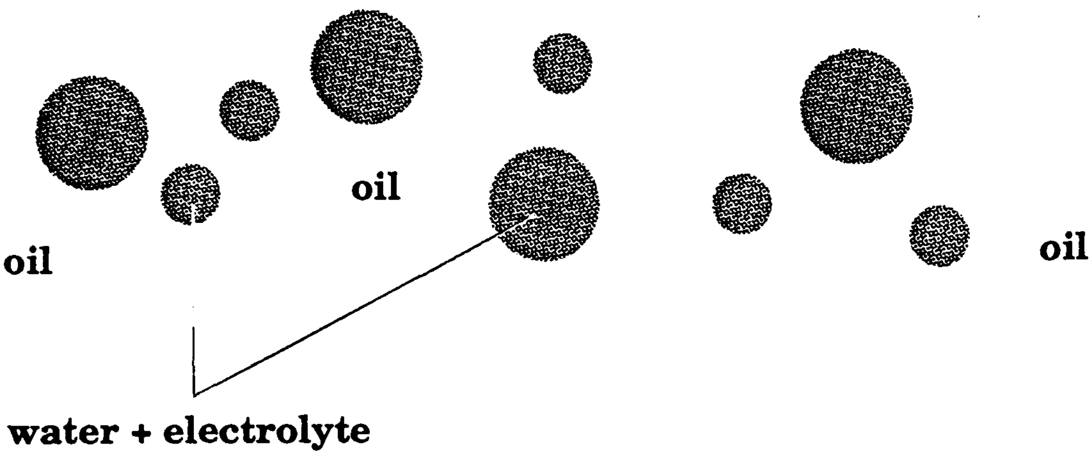
- Using water microemulsions that can dissolve high concentrations of inorganic salts, glasses with up to 70% of inorganic salts can be produced.

- These are unusual new materials with potential as electrolyte and electrode materials for electrochemical technology.

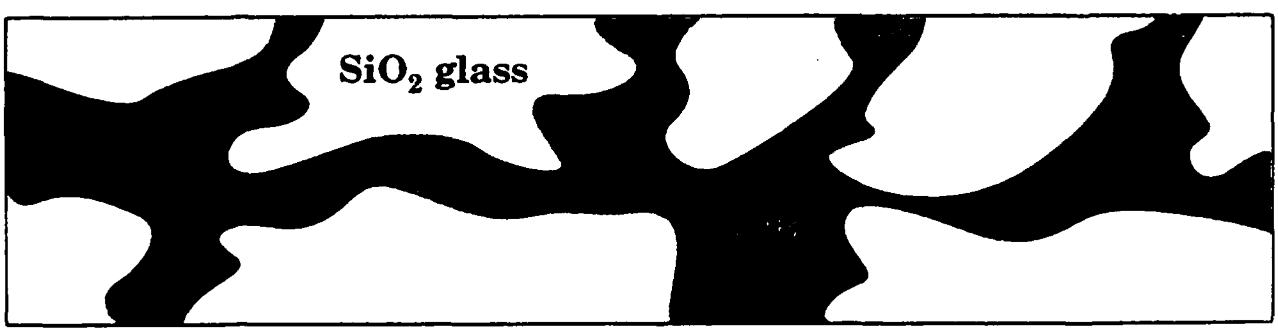
# Forming the Materials from Microemulsions

## The microemulsion:

Water droplets with dissolved electrolyte




After reaction and evaporation the salt is dispersed in the glass giving conduction.




The microemulsion/gel method creates a new kind of material in which any water soluble substance can be introduced in huge amounts (60-70%) into a transparent glass. This is an increase of one order of magnitude in comparision with the traditional process.

# TEM Image of $V_2O_5$ Aerogel

Room Temperature 100 nm

220°C 100 nm

250°C 100 nm

300°C 100 nm